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(54) Title: HIGH REFRACTIVE INDEX AND HIGH IMPACT RESISTANT POLYTHIOURETHANE/UREA MATERIAL, METHOD OF MANUFACTURING SAME AND ITS USE IN THE OPTICAL FIELD

(57) Abstract: A transparent, non elastomeric, high index, impact resistant polythiourethane / urea material comprising the reaction product of : a) at least one (α, Ω)-diiso(thio)cyanate cycloaliphatic or aromatic prepolymer having a number average molecular weight ranging from 100 to 3000 gmol-1, and b) at least one primary diamine, in an equivalent molar ratio amine function / iso(thio)cyanate function from 0.5 to 2, preferably from 0.90 to 1.10, wherein, said prepolymer and diamine are free from disulfide (-S-S-) linkage and at least one of the prepolymer or the diamine contains one or more S atoms in its chain.

HIGH REFRACTIVE INDEX AND HIGH IMPACT RESISTANT POLYTHIOURETHANE/UREA MATERIAL, METHOD OF MANUFACTURING SAME AND ITS USE IN THE OPTICAL FIELD

BACKGROUND OF THE INVENTION

1) Field of the invention

The present invention relates to a rigid, optically transparent, high index, impact resistant polythiourethane/urea material, which is particularly suited for making optical articles such as sun lenses, ophthalmic lenses and protective lenses.

2) Background of the invention

Plastic materials are widely used in the optical field and particularly in the ophthalmic field for their lightness, high impact resistance and tintable capability by immersion in a bath containing an organic dye.

Optically transparent plastic materials having a high refractive index, higher than 1.53, are of major interest since they render it possible to manufacture optical articles such as lenses of lower thickness for an equivalent corrective power (optical power).

Of course, this increase in refractive index of the material shall not be at the expense of the other valuable properties such as transparency and impact resistance of the material.

Preferably, other required properties for the lens material are :

- non yellowness ;
- ability to be treated (by hard coats, primers, ...) ;
- density as low as possible – ageing resistance (especially photodegradation resistance) .

US 6,127,505 discloses a transparent, non-elastomeric, high index, high impact resistant polyurethane material which is a reaction product of :

- a polyurethane prepolymer prepared by reaction of an aliphatic or cycloaliphatic diisocyanate with at least one OH containing intermediate having a rate average molecular weight of from about 400 to 2.000 selected from the group consisting of polyester glycols, polycaprolactone glycols, polyether glycols, polycarbonate glycols and mixtures thereof, in an equivalent ratio of about 2.5 to 4.0 NCO/1.0 OH ; and

- at least one first aromatic diamine curing agent selected from the group consisting of 2,4-diamino-3,5, diethyl-toluene, 2,6-diamino-3,5,diethyl-toluene and mixtures thereof in an equivalent ratio of about 0.85 to 1.02 NH_2/1.0 NCO.

Unfortunately, the polyurethanes obtained have relatively low refractive index, n_D^{25}, of at most 1.53.

SUMMARY OF THE INVENTION

Thus, the aim of the present invention is i.a. to provide an optically transparent, rigid, high index, impact resistant material that would particularly be useful for making optical articles.

By high refractive index material, there is intended in the present invention a material having a refractive index, n_D^{25} higher than 1.53, preferably of at least 1.55 and most preferably of at least 1.57.

The above objective is reached according to the invention by providing a transparent, non elastomeric, high refractive index, impact resistant polythiourethane/urea material comprising the reaction product of :

a) at least one (α, ω)-di-NCX prepolymer in which X represent O or S and having a number average molecular weight ranging from 100 to 3000 g mol^{-1}, said prepolymer being free from disulfide (-S-S-) linkage and

b) at least one aromatic primary diamine in a molar equivalent ratio NH_2/NCX ranging from 0.5 to 2, preferably 0.90 to 1.10, more preferably from 0.93 to 0.95, said aromatic primary diamine being free from disulfide (-S-S-) linkage, and

c) at least one of the prepolymer or the diamine containing one or more sulfur atoms.

The invention further concerns optical articles such as sun lenses, ophthalmic lenses and protective lenses made of the polythiourethane/urea material defined above.

The (α,ω)-diiso(thio)cyanate prepolymer is preferably an (α,ω)-diiso(thio)cyanate cycloaliphatic or aromatic prepolymer and most preferably such a prepolymer containing one or more sulfur atoms in its chain.

These prepolymers can be prepared by reacting an (α, ω)-diol or dithiol prepolymer, preferably further containing at least one sulfur atom in its chain, with one or more cycloaliphatic or aromatic diisocyanate or diisothiocyanate according to the following scheme :

(α, ω)-di-XH prepolymer (I) + cycloaliphatic or aromatic di-NCX (II) ➔ (α, ω)-di-NCX prepolymer (III)

with X = O or S.

The preferred prepolymers (I) are (α,ω)-dithiol prepolymers, further containing at least one sulfur atom in their chains.

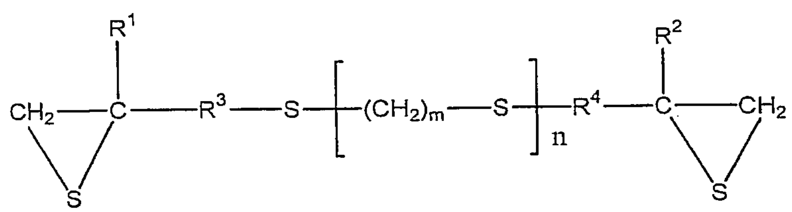
Among these prepolymers there could be cited the following prepolymers :

- Prepolymers of formula :

$$HS-\left[CH(CH_3)CH_2-S\right]_x\left[CH_2CH_2S\right]_y-H \qquad \text{(Ia)}$$

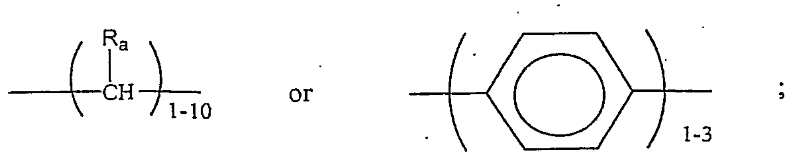
where x and y are such that $\overline{M}_n$ of the resulting prepolymer (III) ranges from 100 to 3000 g mol^{-1} (these prepolymers can be made by polymerizing sulfide monomers, such as ethylene sulfide and 2-mercaptoethyl sulfide (DMES));

- Prepolymers resulting from the polymerization of diepisulfides of formula :



(Ib)

in which R^1 and R^2 are, independently from each other, H, alkyl, aryl, alkoxy, alkylthio or arylthio ; R^3 and R^4 are, independently from each other,



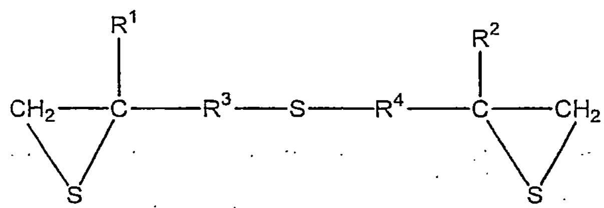
R_a designates H, alkyl, aryl, alkoxy, aryloxy, alkylthio or arylthio and, n is an integer from 0 to 4 and m is an integer from 1 to 6, and

Prepolymers of formula :

$$HS-(CH_2)_2-S-(CH_2)_2-\left[S-(CH_2)_3-S-(CH_2)_3-S-(CH_2)_2-S-(CH_2)_2\right]_n-SH \qquad (Ic)$$

where n is such that the number average molecular weight ($\overline{M}_n$) of the prepolymer ranges from 500 to 1500, preferably from 650 to 1350 g mol^{-1}.

A preferred class of diepisulfides is comprised of diepisulfides of formula :

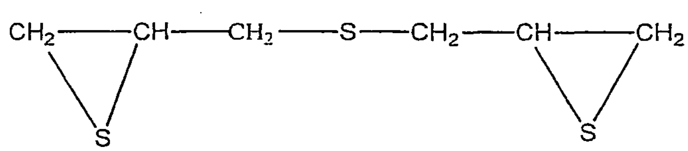


(I'b)

in which R^1, R^2, R^3 and R^4 are defined as above.

In R^1, R^2, R^3 and R^4 the alkyl and alkoxy groups are preferably C_1-C_6, more preferably C_1-C_4 alkyl and alkoxy groups such as methyl, ethyl, propyl, butyl, methoxy, ethoxy, propoxy and butoxy.

The preferred diepisulfides are those of formula :



(I"b)

and hyperbranched prepolymers resulting from the polymerization of the above mentioned diepisulfides, in particular diepisulfides of formulas (I''_b) with DMES.

The prepolymers of formula (I_c) constitute a new class of polysulfides. These new soft polysulfides have high refractive indexes and can be prepared by thermal and/or photopolymerization, in the presence of an initiator, of 2- mercaptoethylsulfide (DMES) corresponding formula

HS-CH_2CH_2-S-CH_2CH_2-SH and allylsulfide (AS) corresponding formula CH_2=$CHCH_2$-S-CH_2-CH=CH_2.

Preferably, prepolymers of formula (Ic) are prepared by photopolymerization in the presence of a photoinitiator.

The refractive index of these prepolymers (I_c) typically ranges from 1.57 to 1.62, preferably from 1.59 to 1.615.

Photopolymerization of prepolymers of formula (Id) is effected by mixing DMES and AS in the required proportions, such that the molar ratio Allyl is less than 2, preferably less than 1 and more preferably less than 0.8, adding at least one photoiniator and irradiating the mixture, preferably with an UV light. Preferably, UV light wavelength will range from 320 to 390 nm. UV light intensity typically ranges from 40 mW to 90 mW and total exposure time to UV light, either in one shot or several shots, ranges from 250 to 1650 seconds, preferably 300 to 1500 and more preferably 600 to 1000 seconds.

Any classical photoinitiator, in usual amount can be used for the photopolymerization process. Preferred photoinitiators are 1-hydroxycyclohexyl phenyl ketone (Irgacure® 184) and 2- hydroxy –2-methyl-1-phenylpropan-1-one (Darocur® 1173). The amount of photoinitiator used will usually range from 0,05 % to 10 % by weight, preferably from 1 % to 5 %, and more preferably from 1 to 2 % by weight, based on the total weight of the polymerizable monomers present in the polymerization mixture.

Although the photoinitiator may be added to the polymerization mixture in one shot, generally before starting irradiation, it is preferred to add the photoinitiator in several shots during irradiation process of the mixture. With the addition of the photoinitiator in several shots, higher conversion rates of the allylsulfide and higher refractive indexes are obtained.

Similarly, thermal polymerisation is effected by simply mixing appropriate amounts of DMES and AS, adding to the mixture an effective amount of at least one thermal radical initiator, and heating the mixture at a temperature ranging from 30°C to 80°C, preferably from 40°C to 70°C.

Any classical thermal initiator can be used, such as di(4-tert-

butylcyclohexyl) peroxydicarbonate (P16S) and 2,2'-azobisisobutyronitrile (AIBN) in usual amounts.

Typically, the amount of thermal initiator will range from 0,05 to 10 %, preferably 1 to 8 %, by weight of the polymerizable monomers present in the mixture.

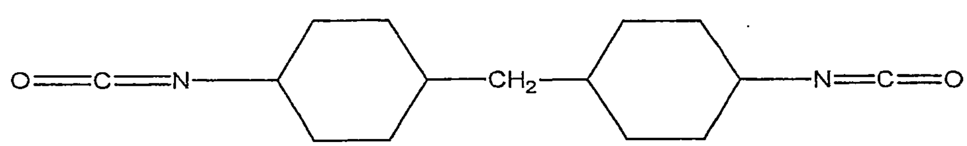
The thermal initiator may be added to the mixture in one shot at the beginning of the polymerisation or in several shots during the course of the polymerization process.

Polymerization is usually effected by bulk polymerization process but it can also be a solution polymerization process using any appropriate solvent or mixture of solvents. A preferred solvent is tetrahydrofuran (THF).

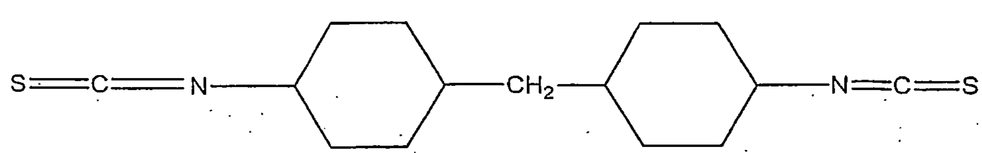
The cycloaliphatic or aromatic diiso(thio)cyanate (II) may be a cycloaliphatic or aromatic diisocyanate or a cycloaliphatic or aromatic diisothiocyanate or a mixture thereof.

Among the preferred cycloaliphatic diiso(thio)cyanate, there may be cited bis(iso(thio)cyanatemethyl) cyclohexane hexamethylene diiso(thio)cyanate and dicyclohexylmethane diiso(thio)cyanate and mixtures thereof.

The most preferred cycloaliphatic diisocyanate is Desmodur® W of formula :



and the corresponding diisothiocyanate of formula :



Among the aromatic diiso(thio)cyanates, there may be cited toluene diiso(thio)cyanate, phenylene diiso(thio)cyanate, ethylphenylene

diiso(thio)cyanate, isopropylphenylene diiso(thio)cyanate, dimethylphenylene diiso(thio)cyanate, diethylphenylene diiso(thio)cyanate, diisopropylephenylene diiso(thio)cyanate, xylylene diiso(thio)cyanate, 4,4'-diphenylmethane diiso(thio)cyanate, naphtalene diiso(thio)cyanate.

The preferred aromatic diiso(thio)cyanate is xylylene diisocyanate (XDI).

The most preferred cycloaliphatic and aromatic diiso(thio)cyanates are Desmodur® W or the corresponding diiso(thio)cyanate or mixtures of these compounds with xylylene diisocyanate.

Usually, the molar ratio NCX/XH of the iso(thio)cyanate group to the hydroxyl or thiol group, during the reaction, ranges from 1.9 to 4.5, preferably from 3 to 3.5.

The reaction of prepolymer (I) and monomer (II) can be effected with or without a polymerization catalyst. Usually, the polymerization is effected at temperature ranging from 50 to 120°C. When no catalyst is used, of course, higher temperatures and longer times of polymerization are required.

Catalyst may be any known catalyst for the polymerization of the monomer.

Among the useful catalysts, there may be cited dimethyltindichloride, dibutyltindichloride and dibutyltindilaurate, cocatalysts or promoters such as N,N –dimethylcyclohexylamine and 1,4 – diazabicyclo – [2,2,2] – octane (DABCO) could also be used with the catalyst to enhance its activity.

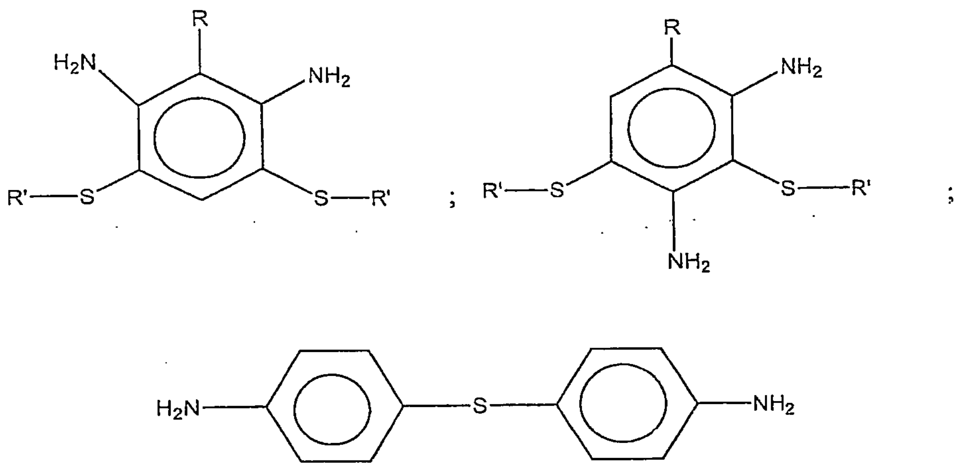
To prepare the final polythiourethane / urea material according to the invention, the (α,ω)-di-NCX prepolymer (III) is reacted with an aromatic primary diamine according to the following scheme :

$$(\alpha, \omega)\text{-di-NCX prepolymer (III)} + \text{aromatic di-}NH_2\text{ (IV)} \longrightarrow \text{final material}$$
$$X = O \text{ or } S$$

During this reaction step, in order to obtain the best properties of impact resistance for the material, it is preferred that the molar ratio NH_2/NCX be kept in the range of 0.90 to 1.10 and preferably 0.93 to 0.95.

Among the aromatic primary diamines (IV) that may be used in the second reaction step, preferred aromatic diamines are those which include at least one sulfur atom in their molecules.

Among these sulfur containing aromatic amines there may be cited the amines of formula :



and mixtures thereof ;

in which R represents a hydrogen atom or an alkyl group, preferably a C_1 to C_6 alkyl group and more preferably a methyl group, and

R' is an alkyl group, preferably a C_1 to C_6 alkyl group, and more preferably a methyl group.

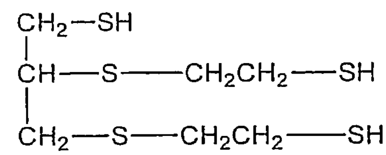
It is possible to replace part of the polyurea segments of the final material by adding one or more of the following monomers to the aromatic diamine in the second step of polymerization.

Thus, a polyurea segment can be replaced by a hard urethane and/or a thiourethane segment by adding a cycloaliphatic or aromatic diisocyanate such as xylylène diisocyanate and/or a diol or a dithiol such as :

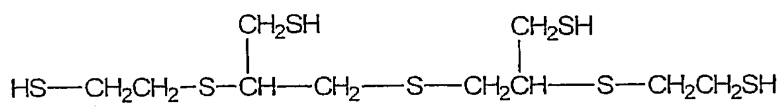
$$HS—CH_2CH_2—S—CH_2CH_2—SH$$

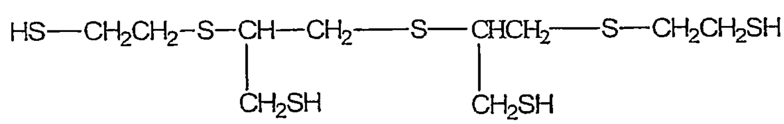
A polyurea segment can also be partly replaced by highly crosslinked areas by adding to the amine during the second step of polymerization tri and tetra alcohols and/or thiols such as :

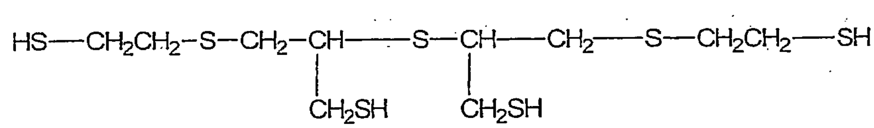
$$C\left(CH_2O-\underset{\displaystyle \overset{\|}{O}}{C}-CH_2CH_2SH\right)_4$$



or polythiols such as those of formula :







and mixtures thereof,

or polyols such as those of formula :

$$HO-CH_2-CHOH-CH_2OH$$

$$HS-CH_2-CHOH-CH_2OH$$

$$HS-CH_2CHOH-CHOH-CH_2-SH.$$

This second reaction step is effected by simply mixing prepolymer (III) with the diamine (IV) and the optional additional monomers, if any, and by heating at a temperature above 100°C, generally ranging from 100°C to 130°C up to the obtention of the final cured polythiourethane / urea material.

Conventional additives such as inhibitors, dyes, UV absorbers, perfumes, deodorants, antioxydants, antiyellowing agents and release agents may be added to the material of the present invention in the usually used quantities.

These additives may be added either in the first step or in the second step of preparation of the final material, but are preferably added during the second step.

The following examples illustrate the present invention. In the examples, unless otherwise stated, all parts and percentages are by weight.

I. Examples of synthesis of polysulfides of formula (I_c)

I.1 Preparation of polysulfides PS1 to PS7.

The polymerization reaction between AS and DMES was carried out in the presence of a photoinitiator, under UV. The equipment used to generate the UV light was an EFOS Ultracure 100 SS PLUS equipped with an optic fiber (lamp # 320-60651).

The UV light was shined above the surface of the monomer mixture. The light intensities reported were measured using a UV-MO2 irradiance meter equipped with a UV-35 sensor (320-390 nm sensing wavelength). Several experimental conditions were studied in order to maximize the refractive index of the reaction product as well as the allyl conversion. The experimental conditions and the results are reported in Table I.

Two photoinitiators were tried : 1-hydroxycyclohexyl phenyl ketone (Irgacure® 184) and 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocur® 1173). As shown in Table 1 (runs PS1 and PS2), a significant increase of the refractive index of the mixture was noticed in both cases. The refractive index of the polymer made was about the same between the two initiators. Darocur® 1173 is a liquid that is easier to handle and to disperse in the monomer mixture than Irgacure® 184 (which is a powder). Thefore, Darocur® 1173 is preferably used in the experiments.

TABLE I

Run	DMES (g)	AS (g)	Photoinitiator (g)	Photoinitiator (%)	Molar ratio Allyl/SH	UV exposure Time (s)	UV Intensity (mW)	n_D(25°C) after UV exposure	Allyl conversion (%)
PS1 a)	10.0102	5.4698	0.3358	2.123	0.738	5x60	51	1.5800	
PS2 b)	9.9916	5.4661	0.1635	1.047	0.739	5x60	51	1.5797	
PS3 b)	10.0305	5.4952	0.3340	2.106	0.740	5x60	51	1.5813	
PS4 b)	9.9961	5.4676	0.8129	4.994	0.739	10x60	40	1.5864 c)	58
PS5 b)	9.9914	5.4658	0.8105	4.982	0.739	10x60	90	1.5869	68
PS6 b)	10.0135	5.4802	5x0.1622	5.075	0.739	5x3+1)x60	50	1.5974 d)	93
PS7 b)	9.9991	5.4674	0.8202	5.036	0.739	960	50	1.5901 d)	76

a) Photoinitiator = Irgacure® 184
b) Photoinitiator = Darocur® 1173
c) $n_D^{25} = 1.5505$ before UV exposure
d) At 40°C, $n_D = 1.5442$ at 40°C before UV exposure

Allyl conversion is measured by FTIR according to the following formula :

$$\text{Allyl conversion (\%)} = 100 \times \left(1 - \frac{\text{Intensity of the } 1636\text{cm}^{-1} \text{ signal/intensity of the } 1672\text{cm}^{-1} \text{ signal after reaction}}{\text{Intensity of the } 1636\text{cm}^{-1} \text{ signal/intensity of the } 1672^{-1} \text{ signal before reaction}}\right)$$

The 1636 cm^{-1} signal corresponds to the allyl group. The 1672cm^{-1} signal corresponds to the phenyl groups of the photoinitiator and was used as an internal reference.

As shown in Table I (PS2 and PS3), the refractive index of the polymer made shows a slight increase when the photoinitiator concentration is varied between 1.0 % and 2.1 %.

The increase of the UV intensity from 40mW to 90mW results in slight increase of the refractive index of the polymer and a higher conversion of the allyl groups (Table I, PS4 and PS5). On the other hand, the increase of the UV exposure time from 600 s to 960 s resulted in a significant increase of both the refractive index and the allyl groups conversion (Table I, PS6 and PS7).

As reported in Table I, PS6 and PS7 where polymerized with the same amount of photoinitiator added to the monomer mixture, either in five shots (PS6) or in one shot (PS7). The results show that the increase of the refractive index of the polymer and the conversion of the allyl groups were much higher when the photoinitiator was added in five shots. Under these conditions, a refractive index (n_D^{25}) of 1.5974 and an allyl conversion of 93 % were reached.

I.2 Preparation of polysulfides PS8 to PS10

The polymerization reaction between AS and DMES was carried out as previously mentioned using the quantities and conditions indicated in Table II. In particular a fusion lamp system equipped with a D Bulb was used for polymerizing PS10.

TABLE II

Run	UV equipment	DMES (g)	AS (g)	Photoinitiator (g)	Photoinitiator (%)	Allyl/SH	n_D(25°C) after UV exposure	Allyl conversion (%)	$\overline{M}$n (g.mol-1)
PS8 b)	Optic fiber	90.10	49.32	5x1.4564	5.065	0.740	1.5790	54	
PS9 b)	Optic fiber	90.11	49.32	5x1.471	5.101	0.740	1.5816	57	
PS10 c)	Fusion system	90.09	49.39	5x1.4470	4.931	0.741	1.6090	98	1080

a) $n_D^{25} = 1.5505$ before UV exposure

b) UV exposure time = 5x180 + 4x180 = 1620 s at 50 mW

c) UV exposure time = 6x(3x70) +180 + 180 = 1620 s at 50 mW

I.3 Preparation of polysulfides PS11 to PS13

The polymerization reaction between AS and DMES was usually carried out in bulk or in the presence of tetrahydrofuran (THF) as a solvent, with the conditions indicated in Table III.

The allyl conversion in the final product was similar to the one obtained in the absence of THF.

TABLE III

Run	DMES (g)	AS (g)	THF (g)	Photoinitiator (g)	Photoinitiator (%)	Allyl/SH	UV exposure Time (min)	n_D^{25} after UV exposure	Allyl Conversion (%)
PS 11	10.0262	5.4818	0	5x0.1613	4.944	0.739	5x3.5	1.6084	97
PS12	10.0262	5.4818	0	5x0.1613	4.944	0.739	5x3.5 + 3x3.5	1.6112	96
PS13	10.0193	5.4799	13.0431	5x0.1649	2.808	0.739	5x (3x1.2)		96

Photoiniator = Darocur® 1173, UV Intensity = 50 mW, Fusion lamp

The SH content of the polysulfides was measured by titration using iodine. As expected, the SH content decreased with the increase of the Allyl/SH molar ratio. When Allyl/SH = 0,5, the end groups consist almost exclusively of SH, and the value of $\overline{M}_n$ calculated from the SH content assuming 100 % SH end groups is very close to the one measured by GPC.

1.5 Preparation of polysulfide PS22

In a 100 ml three necked flask equipped with a magnetic stirrer, a heating mantle, an inlet for an inert gas on one port and a condenser on another port, we introduce 30.2016 g DMES, 16.4094 g Ally sulfide (Allyl/SH = 0.734) and 2.6250 g 2,2'-Azobisisobutyronitrile (AIBN) previously dried, 2,2'-Azobisisobutyronitril (AIBN) received from Monomer-Polymer and Dajac Laboratories, Inc.

The mixture is heated to 65°C. Stirring was continued until the FTIR signal at 1636 cm^{-1} corresponding to the allyl groups disappeared (43 hours). This shows that AIBN is an effective initiator.The refractive index n_D^{25} of the mixture at this time was 1.6092. This product is dissolved in about 46 g of THF, and the solution is precipitated drop-wise in two liter of methanol.

After 24 hours, the supernant methanol solution is removed, and the white precipitate is dried under vacuum at room temperature.

The precipitation yield was about 80 %. The refractive index n_D^{25} of the precipitated polysulfide was 1.6140. Its molecular weight by GPC was $\overline{M}_n$ = 900 gxmol-1 ($\overline{M}_w/\overline{M}_n$ = 1.685). Its SH content measured by titration was 2.157 mmol SH/g ($\overline{M}_n$ = 930 gxmol^{-1} based on (α, ω) SH chains).

Although the polymerization reaction between DMES and AS is successful when using a thermal radical initiator, the UV polymerization is a preferred polymerization method since the reaction times are much shorter (27 minutes in UV polymerization versus 43 hours in thermal polymerization).

II. Example of synthesis of (α, ω)-diiso(thio)cyanate prepolymer (III)

The synthesis of these prepolymers was carried out under a blanket of dry nitrogen, at different temperatures, in the presence or absence of dimethyltindichloride catalyst. Several NCO/SH molar ratios were used. The reaction was followed by infra-red spectrometry for the NCO conversion (NCO signal at 2262 cm^{-1}), Raman spectroscopy for the SH conversion (SH signal at 2520 cm^{-1}) and by measuring the refractive index. After the reaction was stopped (by removing the heat source), the NCO content of the prepolymers was measured by titration.

Starting components, quantities and reaction conditions are given in Table V below.

I.4 Preparation of polysulfides PS14 to PS21 :

All the experiments carried out so far used an Allyl/SH molar ratio of about 0.739. In order to study the effect of this molar ratio on the properties of the polysulfides made, a series of experiments have been conducted where the Allyl/SH molar ratio was varied from 0.500 to 1.354. The experimental conditions as well as the results of these syntheses were reported in Table IV.

As shown, the refractive indexes, the allyl conversion and precipitation yields of the polysulfides were all similar to each other.

The refractive index n_D^{25} was around 1.611 for most the precipitated polymers, which is higher than of the LP-33 polysulfide, a polysulfide having –S-S- linkages from Morton International (n_D^{25} = 1.559).

Structures of the polysulfides were confirmed by H NMR and 13C NMR spectrum.

TABLE IV

Run	DMES (g)	AS (g)	Photoinitiator (g)	Photoinitiator (%)	Allyl/SH	n_D^{25} before UV exposure	n_D^{25} after UV exposure	Allyl conversion (%)	Yield (%)	n_D^{25} of precipitated polymer	$\overline{M}_n$ (g.mol^{-1})
PS 14	10.9512	4.0532	5x0.1602	5.068	0.500	1.5642	1.6072	95	72.1	1.6125	650
PS15	9.7001	5.3094	5x0.1554	4.921	0.740	1.5581	1.6067	90	76.5	1.6122	860
PS16	8.9964	5.9973	5x0.1579	5.002	0.901	1.5488	1.6064	87	80.3	1.6092	1080
PS17	8.6277	6.3654	5x0.1578	5.001	0.997	1.5480	1.6044	80	75.1	1.6106	1100
PS18	8.6247	6.3781	5x0.1597	5.054	0.999	1.5432	1.6032	81	64.8	1.6112	1070
PS19	8.5813	6.4342	5x0.1562	4.944	1.013	1.5464	1.6065	86	74.4	1.6124	1050
PS20	8.2525	6.7829	5x0.1609	5.080	1.111	1.5402	1.6052	84	73.0	1.6105	1120
PS21	7.4855	7.5026	5x0.1583	5.015	1.354	1.5348	1.6058	85	71.0	1.6116	1320

UV exposure = 5x210 s at 50 mW except (6x210 + 180 + 180 s) (Fusion System)

$\overline{M}$n was measured by Gas peak chromatography (GPC)

TABLE V

NCO-terminated prepolymer	Polysulfide	Polysulfide (g)	Desmodur®W (g)	Reaction Temperature (°C)	Reaction Time (hrs)	At the end of reaction % NCO res. (FTIR)	At the end of reaction % SH res. (RAMAN)	n_D^{25} after synthesis
I	PS10	52.10	39.72	110	144	73.8	3.5	1.5760
A	LP-33	146.71	116.09	110	41	75.7	6.5	1.5411

Desmodur® W was provided by BAYER :

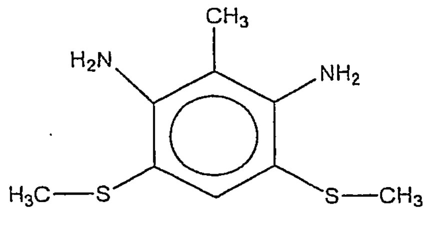
- Physical state : slurry at RT (melting point : 40-50°C)
- Purity (NCO titration) : 97.3% (NCO content measured was 31.2%, 31.8% according to Bayer)
- Refractive index n_D at 45°C : 1.4950
- Specific gravity at 25°C : 1.07

III. Obtention of the polythiourethane / urea material

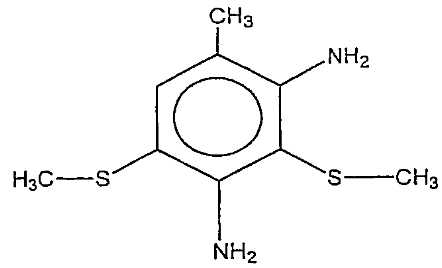
NCO terminated prepolymer 1 obtained in step II above was reacted with Ethacure®-300 (which is a 80:20 mixture of the 2,4- and 2,6- isomers of dimethylthiotoluenediamine), and filled into –2.000 dioptries glass molds to make a lens. The experimental conditions of the casting and the properties of the lense are reported in Tables VI and VII. They show that the use of the polysulfide PS10 allows to reach a refractive index of 1.615, a good impact resistance.

Ethacure®-300 monomer was provided by Albermarle Corporation. It is an approximate 80:20 mixture of the 2,4- and 2,6-isomers of dimethylthiotoluenediamine, and has the following characteristics :

- Physical state : liquid
- Color : clear amber, darkens with time, upon exposure to air
- Refractive index n_D at 25°C : 1.6642
- Specific gravity at 20°C : 1.208
- Viscosity at 20°C : 690 cSt



(2,6-isomer)



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(2,4-isomer)

TABLE VI

	NCO Prepolymer 1. (g)	Ethacure® 300 (g)	Molar ratio NH2/NCO.	Degas Time. (mn)	Degas Temp. (°C)	Mix. Time (mn)	Mix. Temp (°C)	Cure Cycle
Example 1	30.1799	5.9137	0.940	30	110	3	110	8hrs/130°C

Degas : degasing

Mix : Mixing

TABLE VII

Run	NCO Prepolymer	Formulations (Prepolymer + Amine)	NH2/NCO	Index (n_D^{25})	Density	Dynatup Impact / Center thickness of the –2.00 lens	Soft. Temps*	Modulus (E') at 25°C**	Modulus (E') at 100 °C
Example 1	1	83.62% + 16.38%	0.940	1.615	1.21	133 in-lb/1.16 mm (1.532 kg.m)	> 80 °C	8.1×10^8 Pa	1.7×10^8 Pa
Example A (comparative)	A	79.2% + 20.1%	0.931	1.592	1.25	111 in-lb/1.30 mm (1.279 kg.m)	> 80 °C	-	
Example B (comparative)	A	79.86% + 20.14%	0.932	1.592	1.25	160 in-lb/2.10 mm (1.843 kg.m)	> 80 °C	8×10^8 Pa	2×10^8 Pa

* The –2.00 lens had no deformation under a certain force by hand in Oven of 80°C (softening temperature > 80 °C).

** The modulus was measured by DMA.

The results of Table VII show that the material of the invention exhibits both a higher refractive index and high impact resistance.

Impact energy (Dynatup) was measured using an impact test machine designed by General Research Corp. (Model 8210 Drop Weight Impact Test Machine). This machine has the capability to test materials over a wide range of velocities and energies. The velocities can reach up to 4.5 m/sec with a maximum standard drop eight of 36 inches. The cross-head weight can vary from approximately 4.1 to 27 kg.

E' modulus is measured by dynamic mechanical analysis (DMA) using a Perkin Elmer DMA 7e equipment (3-point bending, heat from 5°C to 180°C at 2°C/min and a frequency of 1 Hz).

CLAIMS

1. A transparent, non-elastomeric, high index, impact resistant polythiourethane/urea material comprising the reaction product of :

   a) at least one (α, ω)-diiso(thio)cyanate prepolymer having a number average molecular weight ranging from 100 to 3000 $gmol^{-1}$, said prepolymer being free from disulfide (-S-S-) linkage, and

   b) at least one aromatic primary diamine, in an equivalent molar ratio amine function / iso(thio)cyanate function (NH_2/NCX, X=0,S) ranging from 0.5 to 2, preferably 0.90 to 1.10, said aromatic primary diamine being free from disulfide (-S-S-) linkage, and

   wherein, at least one of the prepolymer or the diamine contains one or more S atoms in its chain.

2. The material of claim 1, wherein said at least one (α, ω)-diiso(thio)cyanate prepolymer is a cycloaliphatic or aromatic prepolymer.

3. The material of claim 1, wherein the equivalent ratio NH_2/NCX ranges from 0.93 to 0.95.

4. The material of claim 2, wherein the (α, ω)-diiso(thio)cyanate cycloaliphatic or aromatic prepolymer is the reaction product of at least one (α, ω) diol or dithiol prepolymer and at least one cycloaliphatic or aromatic diiso(thio)cyanate.

5 The material of claim 4, wherein the (α, ω) diol or dithiol prepolymer contains at least one S atom in its chain.

6. The material of claim 4, wherein the (α, ω) diol or dithiol prepolymer is a polysulfide or a mixture of polysulfides.

7. The material of claim 6 wherein the polysulfide or mixture of polysulfides is selected from the group consisting of :

- Prepolymers of formula :

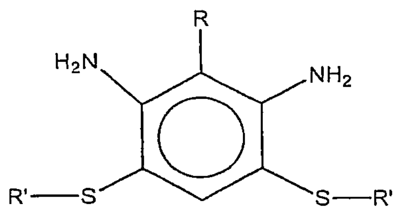
$$HS-\left[CH(CH_3)CH_2-S\right]_x\left[CH_2CH_2S\right]_y-H$$

in which x and y are such that the number average molecular weight of the prepolymer ranges from 100 to 3000 $gmol^{-1}$;

8. The material of claim 6, wherein the polysulfide is an hyperbranched polysulfide .

9. The material of claim 1, wherein the aromatic diamine contains at least one S atom in its molecule.

10. The material of claim 9 wherein the diamine is selected from



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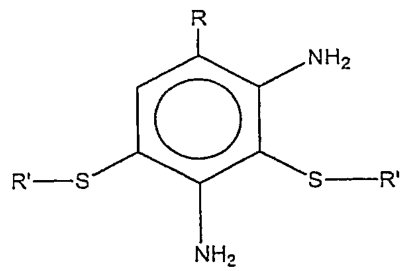

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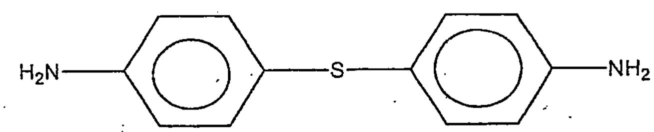
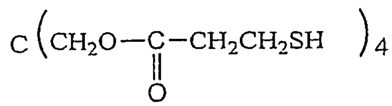


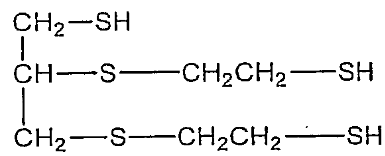
in which R is H or an alkyl group and R' is an alkyl group, and mixtures thereof.

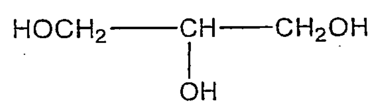
11. The material of claim 1, wherein in step (2) the (α, ω)-diiso(thio)cyanate prepolymer is also reacted with a di-, tri- or tetra alcohol, a di-, tri or tetrathiol or a mixture thereof.

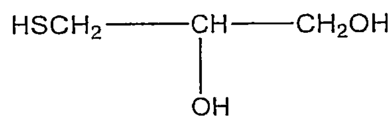
12. The material of claim 11, wherein the di-, tri- and tetra alcohols and thiols are selected from the groups consisting of :

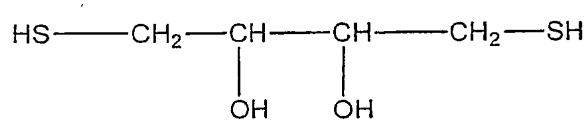
$$HS\ CH_2CH_2\ S\ CH_2CH_2\ SH$$

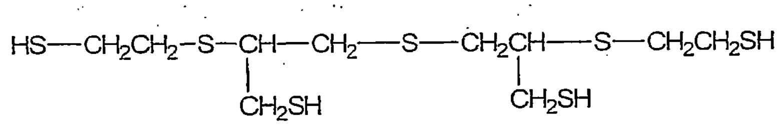


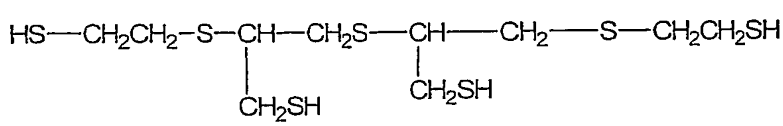


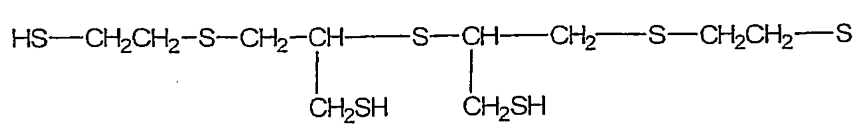












and mixtures thereof.

13. The material of claim 1 having a refractive index, n_D^{25}, higher than 1.53.

14. The material of claim 1 having a refractive index, n_D^{25}, of at least 1.55.

15. The material of claim 1 having a refractive index, n_D^{25}, of at least 1.57.

16. An optical article made from a material according to claim 1.

17. The optical article of claim 16, wherein said article is selected from the group consisting of sun lenses, ophthalmic lenses and protective lenses.

18. Polysulfide of formula :

$$HS-(CH_2)_2-S-(CH_2)_2-\left[S-(CH_2)_3-S-(CH_2)_3-S-(CH_2)_2-S-(CH_2)_2\right]_n-SH$$

wherein n is such that the number average molecular weight of the polysulfide ranges from 500 to 1500 $gmol^{-1}$.

19. The polysulfide of formula 18 having a number average molecular weight ranging from 650 to 1350 $gmol^{-1}$.

20. A process for making a polysulfide according to claim 18, which comprises irradiating with a UV light a mixture of 2-mercaptoethylsulfide and allylsulfide in the presence of a photoinitiator.

21. The process according to claim 20 wherein the photoinitiator is added in several shots during the irradiation process.

22. A process for making a polysulfide according to claim 18, which comprises thermally polymerizing a mixture of 2-mercaptoethylsulfide and allylsulfide in the presence of a thermal initiator.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/12767

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G18/10 C08G18/38 G02B1/04 C08G75/02 C08G75/04
C08G75/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 254 229 A (SCHWINDT JUERGEN ET AL) 3 March 1981 (1981-03-03) example 1	1-17
Y	US 6 100 362 A (NAGATA TERUYUKI ET AL) 8 August 2000 (2000-08-08) column 10, line 50 - line 54 column 18, line 22 - line 24 column 18, line 50 examples 13-47	1-17
A	column 5, line 15 -column 7, line 40	18-22
Y	WO 01 70841 A (ALBERMARLE CORP) 27 September 2001 (2001-09-27) page 4, line 6 -page 5, line 15	1-17

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 March 2003	15 April 2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Müller, M

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 198527 Derwent Publications Ltd., London, GB; Class A26, AN 1985-163618 XP002236322 & SU 1 085 991 A (CONS BUR), 15 April 1984 (1984-04-15) abstract -----	18-22

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Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [ ] Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. [ ] Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. [ ] Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. [X] As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. [ ] As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

[ ] The additional search fees were accompanied by the applicant's protest.

[X] No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-17

   Claims 1 - 17 of the present application refer to a polythiourethane-urea material being prepared from a sulphur-containing component (prepolymer and/or amine). This claim thus embraces numerous alternative embodiments, each embodiment covering one particular sulphur-containing component to be used for preparing the polythiourethane-urea.

2. Claims: 18-22

   Claims 18 - 22 of the present application are directed to a specific sulphur-containing component.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/12767

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
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			DE	69502118	D1	28-05-1998
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			JP	7252207	A	03-10-1995
			KR	180926	B1	15-05-1999
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			EP	1265940	A2	18-12-2002
			WO	0170841	A2	27-09-2001
SU 1085991	A	15-04-1984	SU	1085991	A1	15-04-1984